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THE SYNTHESIS AND PROPERTIES OF A METHYLVIOLOGEN ANALOGUE[1)]

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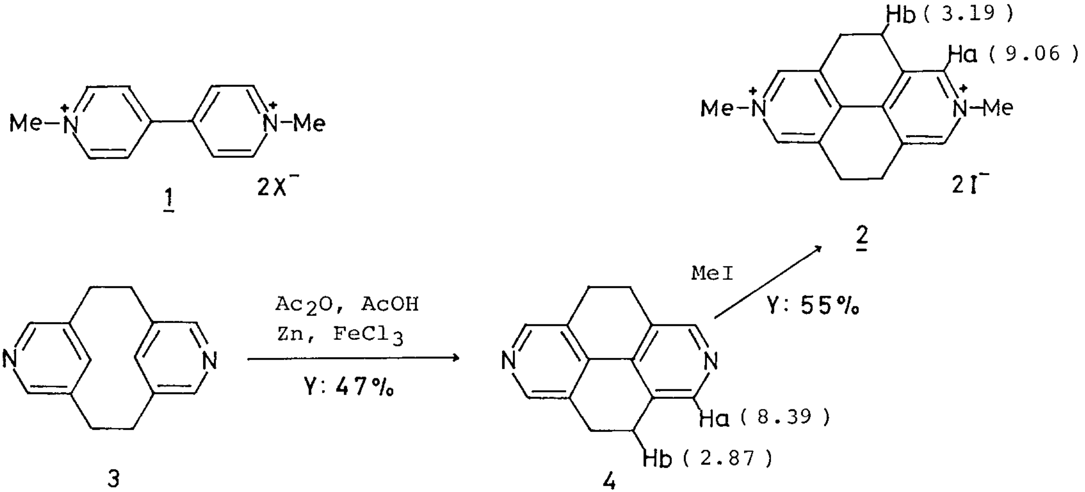
Summary: A novel derivative of methylviologen, prepared by transannular reaction of [2.2](3,5)pyridinophane, shows large bathochromic shift in the electronic spectrum and nearly equal redox potential compared with methylviologen.

Viologen derivatives have been well investigated as an electron mediator for solar energy conversion system. In addition, they have also been studied extensively in the field of synthetic organic metal.[2)] In this communication, we wish to report the synthesis and properties of a new analogue 2 of methylviologen 1.



[The values in parentheses are NMR chemical shift(δppm, 60MHz) in DMSO-d_6]

The target compound 2 was prepared by a synthetic route using a well-known transannular reaction[3)] of pyridine ring as shown in the scheme. The starting material, [2.2](3,5)pyridinophane 3[4)] was prepared by flash pyrolysis of the corresponding cyclic bis-sulfone.[5)] When 3 was treated with acetic anhydride, zinc dust, and $FeCl_3$ catalyst in acetic acid, the transannular reaction took place to produce tetrahydrodiazapyrene 4 [4: colorless plates from acetone, mp 227.5-228.5°C]. Methylation of 4 with methyl iodide in methyl alcohol under reflux for 3 hours gave N,N'-dimethyl-4,5,9,10-tetrahydro-2,7-diazapyrenium diiodide 2 [2: red plates from methyl alcohol, mp > 300°C]. The structure of the viologen derivative 2 was characterized by ^{1}H-NMR and elemental analysis. The NMR data in the reaction scheme indicate that two pyridine ring of 2 were quaternized evidently because of marked downfield shift of Ha and Hb as compared with 4.

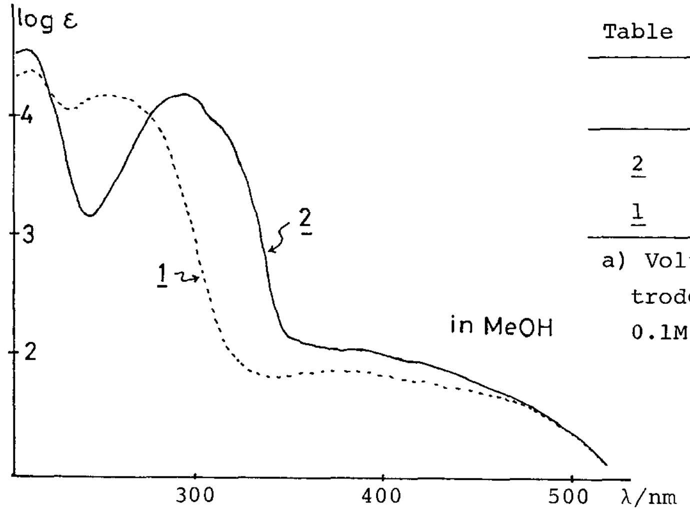


Fig. 1. Electronic Spectra of 1 and 2.

Table 1. CV data of 1 and 2$^{a)}$

	$E^1_{1/2}$/V	$E^2_{1/2}$/V
2	-0.69	-1.03
1	-0.53	-0.90

a) Volts vs. saturated calomel electrode at a glassy carbon electrode ; 0.1M Et_4NClO_4-DMF, scan rate 50mVs^{-1}

As seen in Fig. 1, the electronic spectrum of 2 shows large bathochromic shift(Δλmax 40nm) in the absorption of π-π* transition as compared with that of 1. The fact indicates that the two pyridine rings in 2 are nearly coplanar as expected. Cyclic voltammetry of 2 (Table 1) shows two reversible one-electron reductions. The potential of 2 is slightly different from that of 1, suggesting that the electron-releasing effect of the ethano bridges and the resonance effect due to coplanarity of the two pyridine rings are compensated each other in the electronic nature of 2.

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References

1) The Chemistry of Constrained Hetero Aromatics. I.
2) G.J.Ashwell, G.H.Cross, D.A.Kennedy, and I.W.Nowell, J. Chem. Soc., Perkin Trans. II, 1983, 1787.
3) A.T.Nielsen, D.W.Moore, G.M.Muha, and K.H.Berry, J. Org. Chem., 29, 2175(1964).
4) W.Jenny and H.Holzrichter, Chimia, 21, 509 (1967).
5) T.Otsubo, M.Kitasawa, and S.Misumi, Chem. Lett., 1977, 977.

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